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A BOLOMETRIC STUDY OF ABSORPTION SPECTRA

A THESIS

Submitted For The Degree Of Master Of Science

By

WILLIS FRANK MINIUM

28 April, 1902

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A BOLOMETRIC STUDY OF ABSORPTION SPECTRA

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INTRODUCTORY

The investigation described in the following pages was begun with the expectation of making a detailed study of the infra-red emission spectra of the metals, very little having been done in this line so far as accurate measurements of wave-length are concerned. The time at my disposal proved too short, however, to secure instrumental conditions of sufficient sensitiveness, so I turned my attention to the study of absorption in the regions of infra-red radiation, in which there yet remains much to be done.

A GENERAL REVIEW

The first to detect the presence of radiation beyond the red of the visible spectrum was Sir William Herschel[1], who, in 1800, by placing a thermometer successively in the different colors, discovered an unequal distribution of heat in the prismatic solar spectrum, and noted that a maximum effect was obtained beyond the red. He showed that this

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[1] Phil. Trans., 1800.

radiation obeyed the laws of reflection and refraction exactly as that of the visible spectrum.

Sir John Herschel[1], in 1840, experimenting with strips of paper moistened with alcohol, believed that he discovered the presence of solar absorption bands in the infra-red. Later, in 1842, using plates coated with iodide of silver, Draper[2] found several bands in this region of the solar spectrum; and again, in 1846, these were rediscovered by Fizeau and Foucault[3], who used thermometers of small diameter. Lamanski[4], Mouton[5], and Desains[6] each investigated the distribution of the energy of the solar spectrum by means of a thermopile.

E. Becquerel[7], using a phosphorescent screen, observed the presence and calculated the wave-lengths of these bands. Later, H. Becquerel[8], by means of a similar and somewhat improved method, was able to determine approximately bands of the solar spectrum up to about 14000 Ångström units. His measurements extended also to some metallic lines.

Abney[9], using plates prepared by a special process, photographed the solar spectrum up to about 10000 Ångström units.

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[1] Phil. Trans. 1840.
[2] Phil. Mag., **24**, p. 456, 1842.
[3] C.R., **25**, p. 449. 1847.
[4] Pogg. Ann., **146**, p. 207, 1872.
[5] C. R., **87**, p. 298, 1879.
[6] C. R., **95**, p. 435, 1882.
[7] C. R., **69**, p. 999, 1869; **77**, p.302, 1873; **83**, p. 249, 1876.
[8] C. R., **96**, p. 121, 1883.
[9] Phil. Trans., p.653, 1880.

Among others who have contributed to the investigation of this region are: E. Pringsheim[1], using a Crookes radiometer; Langley, Snow, Rubens and Nichols, and Paschen, using a bolometer; and Lewis[2], using a radiomicrometer.

Langley, working in the infra-red of the prismatic spectrum, having failed to secure sufficient sensitiveness from a thermopile, in 1879 devised the bolometer. This is in principle a Wheatstone bridge, one arm of which indicates temperature changes through varying resistance depending upon the intensity of the incident radiation. Professor Langley has succeeded in affecting improvements in his apparatus, including the galvanometer, until now he claims a sensitiveness such that a change in temperature almost as small as a millionth of a degree is indicated.

Professor Langley[3] has carried on a very complete investigation of the infra-red of the solar spectrum to a wavelength almost as great as 60000 Ångström units. His prisms were calibrated by comparison with the spectrum of the concave grating.

Snow[4] investigated the spectra of the alkali metals with the bolometer. He used a flint glass prism calibrated by means of interference bands produced in the spectrum by thick glass

[1] Wied. Ann., 18, p. **32**, 1883; Phil. Mag., **43**, p. 282, 1872.
[2] Astrophys. Jl., **2**, pp. 1 and 106, 1895.
[3] Ann. Astrophys. Observ. of Smithsonian Institution, **1**, 1900.

plates. This is the same method as described by Rubens[1]. Snow estimated that the sensitiveness of his bolometer was about $\frac{1}{130000}$ of a degree for a deflection of one millimeter on a scale three meters distant.

Rubens and Nichols[2], using a bolometer, have made determinations for "heat rays of great wave-length". They used quartz and fluorite prisms calibrated as indicated in the case of Snow.

Paschen[3] has conducted extensive research in both the prismatic and grating spectra. Fundamental to the latter have been his determinations for the dispersion of fluorite and rock salt in the infra-red. His prisms were calibrated with reference to the spectrum of the concave grating. All of this work has been carried on with the aid of the bolometer.

Bearing more directly upon the substance of this paper, however, is the work of Julius, Ångström, and Paschen.

Julius[4] has investigated the absorption spectra of a number of organic and inorganic substances, including many of the alcohols and ethers, by means of the bolometer.

Ångström[5] has carried on bolometric research in the absorption spectra of carbon dioxide, water vapor, liquid

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[1] Wied. Ann., **45**, p. 238, 1892.

[2] Phys. Review, **4**, p. 314, 1897.

[3] Wied. Ann., **48**, p. 273, 1893; **53**, p. 287, 1894.

[4] Verh. d. Kongl. Akad. d. Wetenschaft. Amsterdam. Del.I, **1**.1892.

[5] Öfversigt Kongl. Vetensk. Akad. Förhändlingar, **46**, p.549, 1889; **47**, p. 331, 1890; Phys. Review, **1**, p. 597, 1892.

ether, benzine, carbon bisulphide, the diamond, and other substances.

Paschen[1], using the same method of investigation, has worked on the absorption spectra of liquid water, water vapor, and carbon dioxide.

INSTRUMENTS AND METHODS

I. THE BOLOMETER

After preliminary experiments in which tests were made of the radiometer, thermopile, seleno-aluminium cell, and bolometer, the latter was chosen as promising to be the best adapted to the study of prismatic spectra in the infra-red.

Platinum has been shown by Langley and Snow to be most serviceable for use as bolometer resistance. Accordingly, a platinum wire having a diameter of 0.025 of a millimeter was flattened and used for this purpose. A framework of brass was set into one end of a cylindrical vulcanite spool, through the length of which was cut a rectangular opening four by seven millimeters. The metal framework (Fig. 1) consists of three plates, one placed below the opening, the other two above and end to end, care being taken as to their complete insulation. From one of the upper plates to

[1] Wied. Ann., **52**, p. 209, 1894; **53**, p. 334, 1894.

the lower was stretched and soldered a fine platinum wire, so that it came opposite the rectangular opening and in the direct path of all radiation. This wire was smoked in a camphor flame. Parallel to it was soldered another similar strip from the second upper plate to the lower. Each of these strips form one arm of a Wheatstone bridge. The plane of these plates being sunk several millimeters below the end of the spool, leaves an outer cylindrical shell of about three millimeters thickness, the end of which is closed by a quartz plate held in place by sealing wax and made air-tight by a coating of shellac. A circular piece of tin foil, with a rectangular slit cut from its center, was pasted over this window and served to protect the second platinum strip from radiation. The outer surface of this end of the spool is threaded to screw into a hollow metal cylinder and this is kept in close contact with a tank of water of constant temperature, as is explained more fully below. Deep in the other end of the spool is set a glass plate, and into the open end beyond slides the eyepiece. From the space between the glass and quartz plates a tube leads forward and terminates in a glass stop-cock. This device permits of the

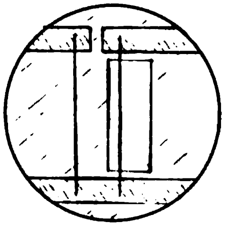

Fig. 1.

exhaustion of the space immediately surrounding the bolometer strips. A wire from the lower brass plate passing through the body of the spool terminates at a binding post in front. This forms one connection with the galvanometer. Similarly, two wires, one from each of the upper plates, terminate at binding posts, forming connection with the battery, while a wire from a fourth binding post is soldered to the middle of an insulated German silver wire wound non-inductively upon the outer surface of the vulcanite spool, and each end is soldered to one of the upper brass plates. This wire furnishes the remaining two arms of the bridge. The outer surface of the whole forms a smooth cylinder which fits snugly into an opening in a copper tank, filled with water, thus insuring a constant temperature. The arrangement as described is represented in Fig. 2, in vertical section, and the general

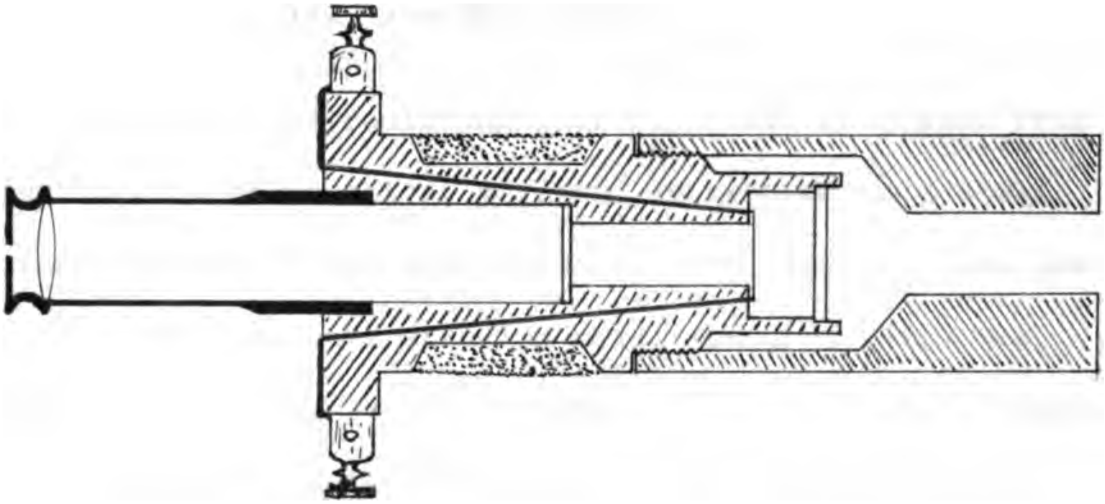

Fig. 2.

plan of the spectrometer in Fig. 3.

To balance the bridge a liquid resistance, capable of minute variation, and used as a shunt between one of the galvanometer and one of the battery terminals, was found to give excellent service. A diluted solution of copper sulphate, contained in a glass tube one hundred and twenty-five centimeters long and twelve millimeters interior diameter, provided with copper terminals, one fixed, the other sliding, gave entire satisfaction.

II. THE SPECTROMETER

Light from the radiating source, after reflection from two large concave silver mirrors, is brought to a focus upon the slit of the spectrometer. Then, falling upon the surface of a concave speculum metal mirror of 48.5 cms. focal length, the pencil of parallel light passes through the prism, and, after reflection from a second similar metal mirror, is brought to a focus upon the cross hairs.

The fluorite prism is so mounted that it may be rotated about a vertical axis by means of a tangent screw and its angular displacement read directly from a divided circle.

A method due to Fuchs for obtaining minimum deviation is employed. The beam, which is reflected at the surface

of a plane silver mirror, placed vertically and at right angles to the bisecting plane of the angle of the prism, and continues in its new path parallel to the old, is the one which passes at minimum deviation. It must, then, be such a pencil of light that falls upon the cross hairs.

A dispersion curve was drawn for the prism, based upon values calculated from data due to Paschen, and Rubens, and all wave-lengths have been referred to this curve.

III. THE GALVANOMETER

An astatic system composed of six small magnets each about 1.5 mm. long, made from No. 19 piano wire steel, was found to give better results than were obtained when more magnets of the same kind or various combinations of

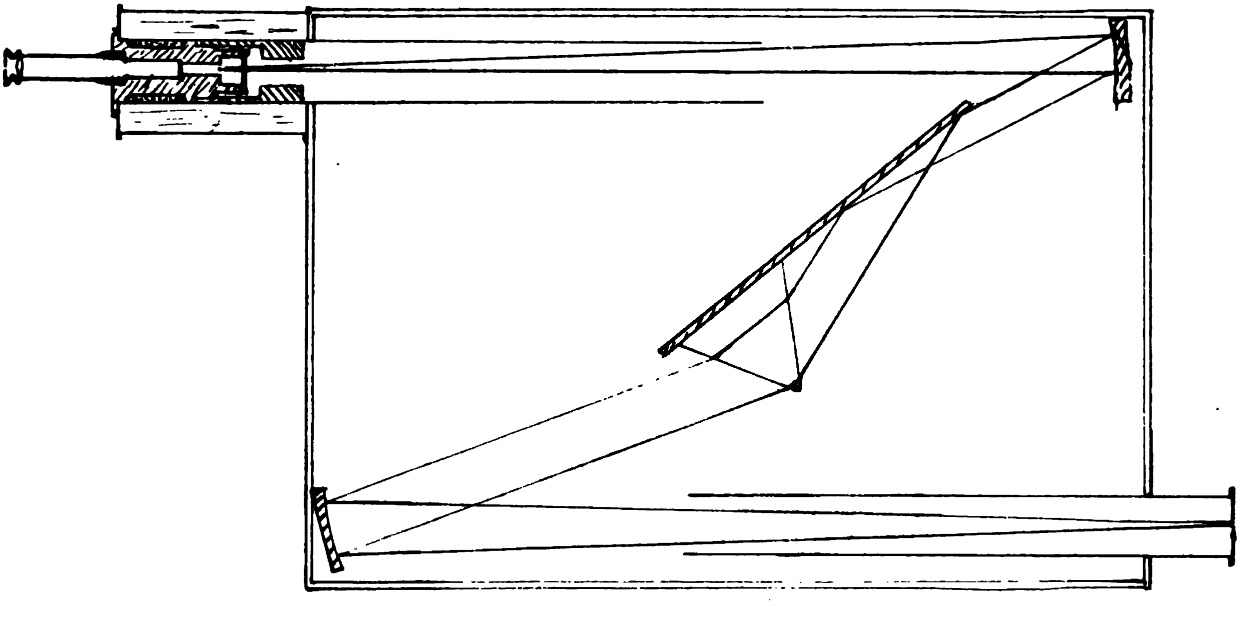

Fig. 3.

other magnets, made either from needle, saw, or watch spring steel were used.

The piano wire was first flattened slightly by hammering, then held in a bunsen flame until cherry red, when it was suddenly cooled in water. Six short pieces, each one and a half millimeters long, were broken from the hardened wire and mounted upon four thin films of mica three millimeters long and one and a half millimeters wide. Two of these pieces of steel were mounted with shellac at opposite ends of one sheet of mica and a third at the middle of a second sheet. The remaining three pieces were mounted in a similar manner. These were then magnetized between the poles of a powerful electro-magnet and mounted on the axis of a slender glass fiber so that each end contained three magnets, producing an approximately astatic system. The system was made yet more astatic by gently twisting the two groups of magnets until their magnetic planes more nearly coincided, by weakening the stronger group, and by using a control magnet. Midway between the two groups of magnets was mounted a small plane mirror.

As a suspension for the needle a very fine quartz fiber, thirty centimeters in length, was used. The method of making these fibers will be described in detail later.

The coils of the galvanometer were constructed on the same general principle as those of Snow. They are four in number, made of three sizes (Nos. 24, 30, and 34) of bare copper wire closely wound and insulated by soaking in melted paraffine. Their resistance when joined in series is about 25 ohms. The distance between the surfaces of two adjacent coils is three millimeters. Two of the coils are embedded in a wooden block which is hinged at the bottom to form a door, thus making the interior of the galvanometer easy of access.

The sensitiveness of the galvanometer to thermal changes was determined by a method similar to that described by Rubens and Ritter.[1] Two shunts containing known resistances were placed in parallel arc with the bolometer arm upon which the radiation fell. The bridge was balanced and the zero of the galvanometer noted. Then, varying the resistance of one of the shunts by a known amount, the corresponding deflection was registered. From this the change in resistance necessary to produce a deflection of one millimeter was calculated. Then taking the temperature coefficient of the platinum as 0.003, the change in temperature necessary to produce a deflection of one millimeter was found. The sensitiveness as determined was 0.00028°C.

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[1] Wied. Ann., **40**, p. 62, 1890.

IV. ON DRAWING QUARTZ FIBERS

It was early discovered that the ordinary silk fiber used for the suspension of the magnetic system was unsatisfactory, and an attempt to secure a suitable thread of quartz was made necessary. The method adopted is similar to that described by Threlfall in his "On Laboratory Arts", and commonly known as the "bow and arrow" method.

The gun was of the ordinary type except that a bow of special quality was employed, the material of which is unknown to me, although it is a close-grained wood resembling very much the olive. It is said to have been taken from the natives of the South Sea Islands.

The chief difficulty encountered in this connection was in the construction of an arrow adapted to the purpose. It is essential that it should be as light as possible and yet firm enough to withstand the shock of impact at the target. The arrow finally used fulfilled these conditions to a fair degree. It was made of Spanish cedar, which is both a reasonably firm and fairly light timber. It was tipped with a short pointed piece of wire nail, just heavy enough to balance the attachments of the other end and throw the center of mass of the arrow somewhat ahead of its geometrical center. To the other end was fastened a thin rod [illegible] 12

of quartz about two inches long which had previously been melted and moulded in the electric arc. This attachment must not be made rigid, since the blow upon striking would be communicated directly to the rod, usually breaking it. A spiral spring of brass about three millimeters in diameter and two centimeters long was made. One end of this was slipped into a closely fitting rubber tube of about two centimeters length and two millimeters diameter, and the other end fastened by two small staples to the top of the arrow. A rod of quartz, one end of which was slightly larger than the other, to fit snugly, was forced into the other end of the tube; and the arrow was complete.

A simple trigger was made to be manipulated by the foot, so that the hands were left free for the remaining adjustments. It consisted in a treadle and string attached through a lever to a wire nail supporting a bow string.

A horizontal arc, one carbon dipping slightly below the other and adjusted at the right height, was set directly behind the bow-gun and the arrow placed in position so that the portion of the quartz rod to be melted occupied the proper position with reference to the carbons of the arc. The end of the rod was grasped firmly with a pair of pliers, and with the foot on the treadle, the arc was "made"

Mr. W. R. Stamper, the department mechanician, who suggested several improvements of construction. This device has proved very efficient, the drift being brought under almost complete control.

Throughout the series of experiments not the final deflection, but the first throw of the galvanometer needle was recorded. This has been justified through an investigation of Professor Merritt[1], who has shown that the first throw of a galvanometer needle, when due to thermal changes in a bolometer or thermopile, bears a constant ratio to the permanent deflection and may, therefore, be taken proportional to the heat radiated.

In order to effect the adjustment of the instrument for minimum deviation, the plane silver mirror was placed against the back surface of the fluorite prism so that it occupied a position approximately perpendicular to the bisecting plane of the angle of the prism. Then, placing the whole upon the table of a spectrometer, the angle between the surface of the mirror and that of the prism was measured and a careful adjustment made until the mirror was fixed in its true position. The prism was then placed upon the table of the spectrobolometer and by means of the reflection of a candle flame at its

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[1] Am. Jl. of Sci., **41**, p. 422, 1891.

surface through the slit of the collimating tube, the prism's face was adjusted perpendicularly to the incident light. From Paschen's value for the refractive index of fluorite for the D-lines, the angle of incidence to produce minimum deviation for these lines was calculated and the prism moved through an angular distance to correspond. It now remained only to adjust the second speculum metal mirror until the D-lines fell upon the cross hairs.

THE INTENSITY CURVE OF INCANDESCENT CARBON

By means of two concave silver mirrors, the image of the positive carbon of the arc lamp was projected upon the slit of the spectrometer, directly in front of which was placed a screen which could be raised or lowered to cut off or admit the light at will. The width of the slit throughout the series of experiments was kept at 0.3 mm.

The intensity of the radiation falling upon the cross hairs was found to vary considerably from one moment to another, due to the changing position of the image at the slit caused by the gradual consumption of the carbons and an effort to recover their former position. It was therefore decided to make observations by pairs under as nearly similar conditions as possible, taking the mean of several readings for each, and then to make

From an examination of this curve (the outer one in Fig. 4) it is at once apparent that the maximum intensity falls without the visible spectrum and in the infra-red. Three regions of absorption are also noted with their minima at about 2.0μ, 2.7μ, and 3.8μ. These minima correspond to Paschen's observations on absorption due to water vapor and carbon dioxide.

ON THE ABSORPTION OF ALUM

I. HISTORICAL

Abney and Festing[1] in 1885 carried on a series of investigations of a number of substances, including alum, and drew their thermograms. The source was an incandescent lamp whose radiation was analyzed by a glass prism, passing through two glass lenses before falling upon a thermopile. A glass-walled cell was used to contain the liquid. Their observations on alum led them to conclude that , in the least refrangible part of the spectrum, the thermogram differs very little from that of water, except that there is a general tendency to intensify the absorptive power of the water in which it is dissolved. In conclusion, they observe, "It may be said that, roughly, one thickness of a saturated solution of alum in water is equivalent to a double thickness of water, and not more."

[1] Proc. Roy. Soc. Lon., **38**, p.77-83, 1885.

Tyndall[1] has undertaken to show that the alum solution is not, as had been generally accepted, wholly opaque to infra-red radiation. His method may be outlined as follows. He assumes that the tests made by him on the diathermacy of a solution of iodine in carbon bisulphide are correct, and that there is no obstruction to infra-red radiation. Such a solution, contained in a rock salt cell, was placed in front of an electric lamp, "the luminous rays being thereby intercepted". Behind this was placed another cell, this of glass. The intensity of the radiation passed by both was registered by a galvanometer deflection of 80°. An alum solution was then poured into the empty cell and the deflection again noted. It was 50°. His conclusion is stated as follows: "Calculating from the values of these deflections, it is found that of the obscure heat emergent from the solution of iodine 20 per cent. was transmitted by the alum".

S. Bidwell[2] allowed the radiation from a paraffine lamp, after passing through a glass-walled cell, at first empty, then containing a solution of alum, to fall upon a delicate thermopile. His results are:

Medium	**Diathermacy**
Empty cell	1000
Water, distilled	197
Water from tap	200
Alum, saturated solution	204

[1] Heat as a Mode of Motion, p. 464.

From this Bidwell concludes that "plain water will answer the purpose of an absorbent rather better than an alum solution".

T. C. Porter[1], using the electric arc as the radiating source, a glass-sided cell as the containing vessel, and a Crookes radiometer for measurement of transmitted heat energy concluded that distilled water is superior to the alum solution in diathermacy. His conclusion is based on the following data:

	No. of revolutions of radiometer arms	**Time in half seconds**
1 Unimpeded radiation	25	160
2 Through empty cell	25	254
3 Unimpeded radiation	25	152
4 Cell + water	25	820
5 Unimpeded radiation	25	164
6 Cell + water	25	832
7 Unimpeded radiation	25	160
8 Cell + alum solution	25	43200
9 Unimpeded radiation	25	160

C. C. Hutchins[2] prepared a cell whose sides were plates of quartz. Into this he put first a solution of alum, then a quantity of water. His "heat measuring apparatus" was so placed as to be affected by whatever radiation passed through the cell from a naked gas jet. A galvanometer indicated the intensity of transmitted radiation. No prism was used and only total radiation measured. The mean of ten deflections in each case was taken; for the alum solution 201, for the pure water 196 degrees. From this Mr. Hutchins concludes that water, if any-

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[1] Nature, **45**, p. 29, 1891.

[2] Am. Jl. Sci., **43**, p. 526, 1892.

thing, is a slightly better absorber than an alum solution.

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II. OBSERVED

In a manner exactly similar to that by which the distribution of the intensity of the incandescent carbon was determined, an intensity curve for the radiation transmitted by a saturated solution of alum has been obtained. In order that the different sets of readings may be directly compared, the observed deflections were reduced to the same proportionality. This was accomplished by taking the readings in pairs, first with the unobstructed radiation, then with the water and cell before the slit, and under as nearly similar conditions as possible. By simple calculation a column of data was obtained from which a curve in every way comparable with the first may be drawn. Similarly, pairs of readings were taken with water and the alum solution and another curve plotted from data reduced in the same way. These curves are shown in figure 4. The middle one is for water and the inner one for alum. The bolometer was passed through the region from 2.75μ up to 4μ but no effect was observed.

It is evident from the diagram that, aside from a slight general absorption, the solution of alum shows no characteristics which are not exhibited by the water itself.

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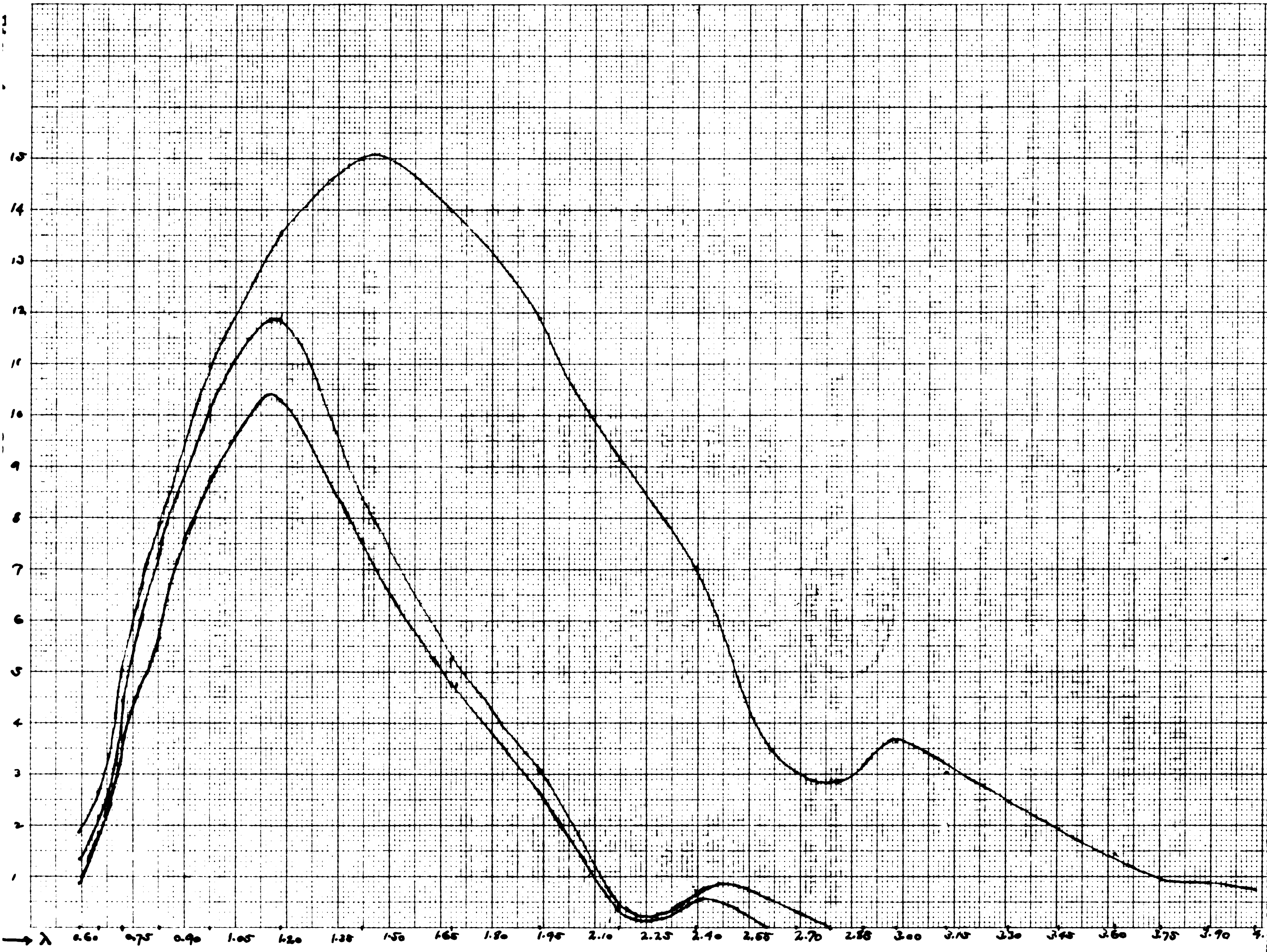

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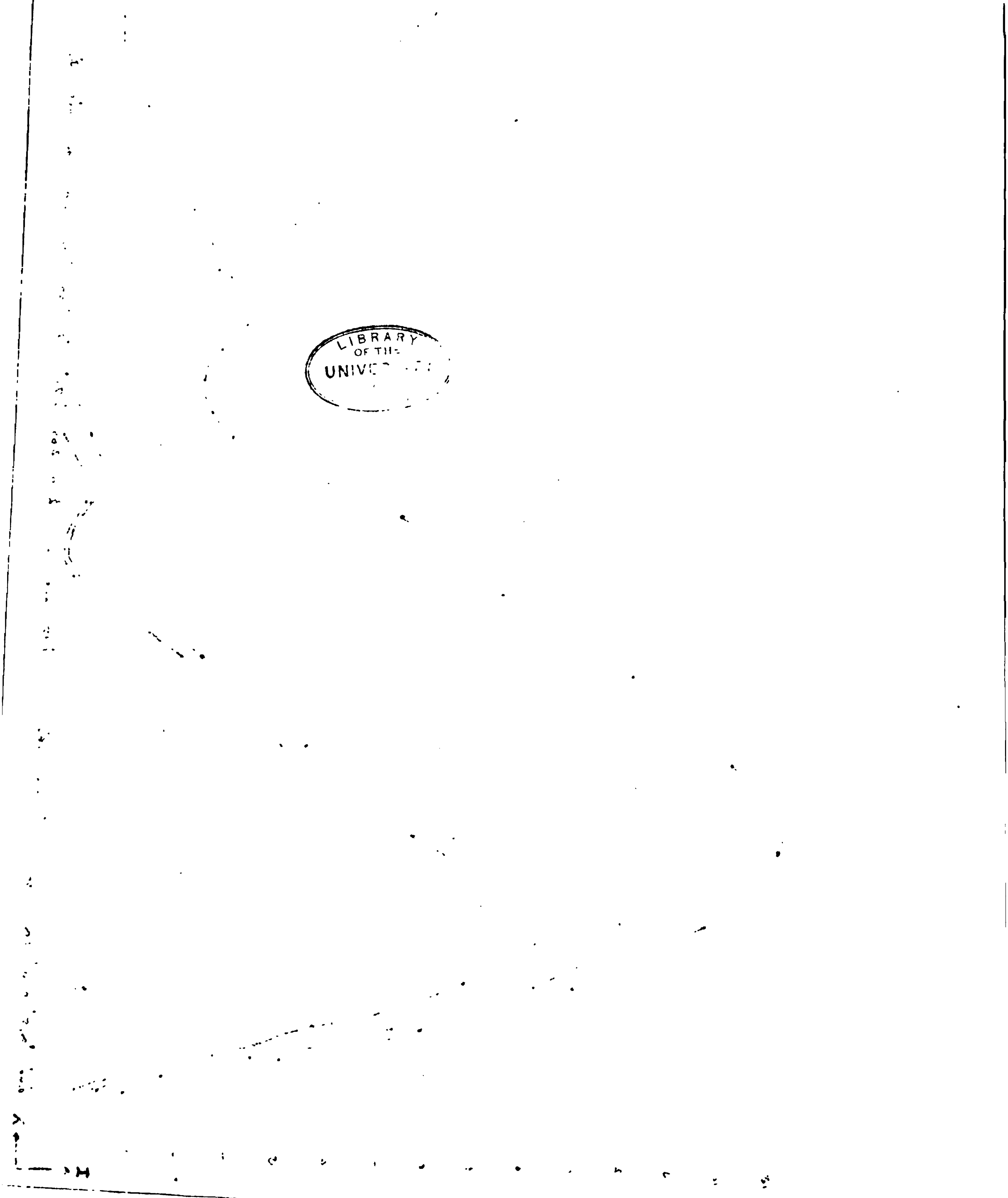

The following table contains the data, reduced from the observed deflections for comparison. Column (1) contains the angular displacements of the prism, column (2), the corresponding value for the wave-lengths, column (3), the proportional intensities for radiation transmitted through water, and column (4), the same for radiation transmitted through the alum solution.

Scale reading	**Wave-length**	**Intensities for water**	**Intensities for alum**
5.20	5893	1.334	0.889
5.15	6463	2.182	1.851
5.10	7188	4.420	3.648
5.05	8272	7.300	5.638
5.00	9750	10.155	8.704
4.95	11810	11.858	10.282
4.90	14200	8.380	7.511
4.85	16800	5.282	4.772
4.80	19404	3.039	2.612
4.75	21699	0.456	0.342
4.70	23950	0.643	0.505
4.65	26006	0.508	0.000
4.60	26877	0.000	0.000

ON THE ABSORPTION OF IODINE

I. HISTORICAL

Among other substances, Abney and Festing[1] made observations on the diathermacy of a solution of iodine in alcohol. They drew

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[1] Proc. Roy. Soc. Lon., 38, pp. 77-83, 1885.

intensity curves (thermograms) showing the distribution of energy. As in the case of alum, the source was an incandescent lamp, and the radiation was analyzed by a glass prism and detected by a thermopile. The cells used were also glass. The thermogram for a "deep-colored solution of iodine" in alcohol showed a slight dip "coincident in position with the alcohol radical band". The thermogram for clear alcohol was found to be "the same as that of the iodine solution in alcohol with the exception that some further thermal action in the visible part had to registered."

Tyndall[1], using a cell with walls of rock salt as a containing vessel and a platinum wire heated white by an electric current as his source, concluded that iodine was perfectly transparent throughout all the infra-red region. He used no analyzing prism and the intensity of radiation was determined by a thermopile.

II. OBSERVED

In a method very similar to that employed in the case of alum, observations were made for the intensity of radiation transmitted by a solution of iodine in alcohol relative to

[1] Heat as a Mode of Motion, p.436.

that transmitted by alcohol itself. The iodine in solution showed remarkable transparency, as is shown by the fact that the deflections throughout that portion of the spectrum covered (up to 3μ) were identical for the two. There was not even a general absorption additional to that of the alcohol.

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